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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

Transmitted herewith for filing under 37 CFR §1.53(c) is the PROVISIONAL APPLICATION for patent of

INVENTOR(S)		
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Hans	Steiner	Basel, Switzerland

TITLE OF THE INVENTION (280 characters max)

COMPOSITION AND METHOD FOR THE PROTECTION OF INDUSTRIAL MATERIALS

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ENCLOSED APPLICATION PARTS *(check all that apply)*

- ☒ Specification (Including Any Claims and Abstract) - 15 pages
- ☐ Drawings - sheets
- ☐ Other (specify):

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Respectfully submitted,

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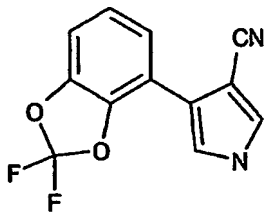
Date: November 26, 2003

Composition And Method For The Protection Of Industrial Materials

The invention relates to the use of phenylpyrrole derivatives as microbicides for the protection of industrial materials.

In particular, the present invention relates to the use of A) the compound 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile (fludioxonil) as a microbicide for the protection of industrial materials, to novel mixtures containing such compound, and to the use of such mixtures for the protection of industrial materials.

The compound A), fludioxonil, is represented by the formula (I)



(I)

This compound, its synthesis as well as is antimicrobial properties are described in U.S. patent 4,705,800, which is incorporated herein by reference.

In one embodiment, the active compound A) of the formula (I) is mixed with at least one other antimicrobially active substance B) to increase the spectrum of action or to achieve particular effects such as, for example, allowing the application rate of the fungicides to be reduced while still maintaining an equally good fungicidal activity, or that identical application rates of the fungicides result in a greater activity than the activity to be expected from the individually employed active substances. In many cases, this results in synergistic effect, that is to say, the activity of the mixture is greater than the activity of the individual components.

Suitable antimicrobially active substances B) for the compositions and methods of the invention are, for example, the following compounds: Azaconazole, bitertanol, bromuconazole, cyproconazole, diclobutrazol, difenoconazole, diniconazole, diniconazole-m, epoxiconazole, etaconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, furconazole, furconazole-cis, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole fumarate, paclobutrazol, pefurazoate, penconazole, propiconazole, prothioconazole, quinconazole,

simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, and uniconazole-p.

The antimicrobially active compounds, when appropriate, may be independently used in the compositions or methods of the invention as stereochemical mixtures or stereochemical isomers.

In addition, the antimicrobially active compounds may be independently employed in the compositions or methods of the invention in free form or, if appropriate, in salt form. Suitable salt forms include addition salts, metal complexes and solvates.

As used herein, the following terms have the designated definitions, unless the context clearly indicates otherwise. The terms "microbicide", "microbicidal" and "antimicrobial" refer to a compound capable of inhibiting the growth of or controlling the growth of microorganisms at a locus; microbicides include bactericides, fungicides and algaecides. The term "microorganism" includes, for example, fungi, yeast, bacteria and algae. The term "industrial material" refers to a non-live material such as an "engineering material", "wood", leather, or other non-live material subject to contamination by microorganisms.

"Engineering materials" or products according to the invention include, for example, non-live materials (other than natural substances of plant or animal origin such as leather, wood or wood products) which have been prepared for use in engineering. For example, engineering materials which are intended to be protected by the active compounds from microbial change or destruction can be glues, sizes, paints and plastic articles, cooling lubricants, aqueous hydraulic fluids and other non-live materials which can be infested with, or decomposed by, microorganisms. Parts of production plants, for example cooling-water circuits, which may be impaired by the multiplication of microorganisms may also be mentioned from amongst the materials to be protected.

For example, the active compound A), mixtures of A) and B), or microbicidal compositions or concentrates containing them can be used to inhibit the growth of microorganisms by introducing a microbicidally effective amount of the compositions onto, into, or at a locus of an engineering material or product subject to microbial attack. Suitable loci include, for example: cooling towers; air washers; boilers; mineral slurries; wastewater treatment; ornamental fountains; reverse osmosis

filtration; ultrafiltration; ballast water; evaporative condensers; heat exchangers; plastics; emulsions; dispersions; paints; latexes; coatings, such as varnishes; construction products, such as mastics, caulks, and sealants; construction adhesives, such as ceramic adhesives, carpet backing adhesives, and laminating adhesives; industrial or consumer adhesives; photographic chemicals; printing fluids; household products, such as bathroom and kitchen cleaners; cosmetics; toiletries; shampoos; soaps; detergents; industrial cleaners; floor polishes; laundry rinse water; metalworking fluids; conveyor lubricants; hydraulic fluids; petroleum processing fluids; fuel; oilfield fluids, such as injection water, fracture fluids, and drilling muds; agriculture adjuvant preservation; surfactant preservation; medical devices; diagnostic reagent prservation; food preservation, such as plastic food wrap; pools; and spas.

Certain compositions containing the active compound A) and certain mixtures of the active compounds A) and B), or microbicidal compositions or concentrates containing them, are employed for protecting industrial materials that are natural substances of plant or animal origin such as leather, leather products, wood, wood products and derived timber products against microorganisms, for example against wood-destroying or wood-discolouring fungi.

"Wood" is to be understood as meaning wood and wood products, for example, pulp and paper processing fluids; wet-lap ("wet-lap" refers to paper or other cellulosic product that is not completely dried after manufacture), derived timber products, lumber, plywood, chipboard, flakeboard, laminated beams, oriented strandboard, hardboard, and particleboard; paper food wrap, tropical wood, structural timber, wooden beams, railway sleepers, components of bridges, jetties, vehicles made of wood, boxes, pallets, containers, telegraph poles, wooden fences, wooden lagging, windows and doors made of wood, plywood, chipboard, joinery, or wooden products which are used, quite generally, for building houses or decks, in building joinery or wood products that are generally used in house-building, construction and carpentry.

The protection of wood is particularly effective when large-scale impregnating treatments, for example vacuum, double vacuum or pressure treatments, are used.

In one embodiment, the present invention relates to antimicrobial compositions comprising fludioxonil and a compound B1): Azaconazole, bitertanol, bromuconazole, diclobutrazol, diniconazole, diniconazole-m, epoxiconazole, etaconazole,

fenbuconazole, flusilazole, flutriafol, furconazole, furconazole-cis, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole fumarate, paclobutrazol, pefurazoate, penconazole, propiconazole, prothioconazole, quinconazole, simeconazole, tetraconazole, triadimefon, triadimenol, uniconazole, and uniconazole-p.

In another embodiment, the fludioxonil compositions are used for the protection of wood or wood products and are substantially free of quaternary ammonium compounds, difenoconazole and tebuconazole.

In a further embodiment, fludioxonil is combined with at least one compound B2): cyproconazole, propiconazole, triticonazole and fluquinconazole. Compositions of A) and cyproconazole or propiconazole are particularly suitable for use in the protection of wood or wood products.

In another embodiment, the present invention relates to antimicrobial compositions that consist essentially of fludioxonil or fludioxonil and at least one compound B1).

In yet another embodiment of the invention, fludioxonil is combined with tebuconazole for use in the protection of engineering materials.

Surprisingly, fludioxonil A) when used alone or in combination with at least one of the active compounds B) displays a particularly powerful microbiocidal activity against microorganisms which are relevant in the protection of industrial materials. Microorganisms which can effect a degradation or change of the industrial materials which may be mentioned by way of example are bacteria, fungi, yeasts, algae and slime-forming organisms. The following groups of microorganisms may be mentioned by way of example, but without imposing any limitation: Wood-discolouring fungi – including *Ascomycetes*; *Ceratocystis* such as *Ceratocystis minor*; *Deuteromycetes*; *Aspergillus* such as *Aspergillus niger*; *Aureobasidium* such as *Aureobasidium pullulans*; *Dactylium* such as *Dactylium fusarioides*; *Penicillium* such as *Penicillium brevicaule* or *Penicillium variabile*; *Sclerophoma* such as *Sclerophoma pithyophila*; *Scopularia* such as *Scopularia phycomyces*; *Trichoderma* such as *Trichoderma viride* or *Trichoderma lignorum*; *Zygomycetes*; *Mucor* such as *Mucor spinorus*. Wood-destroying fungi - *Ascomycetes*; *Chaetomium* such as *Chaetomium globosum* or *Chaetomium alba-arenulum*; *Humicola* such as *Humicola grisea*; *Petriella* such as *Petriella setifera*; *Trichurus* such as *Trichurus spiralis*;

Basidiomycetes; *Coniophora* such as *Coniophora puteana*; *Coriolus* such as *Coriolus versicolor*; *Donkioporia* such as *Donkioporia expansa*; *Glenospora* such as *Glenospora graphii*; *Gloeophyllum* such as *Gloeophyllum abietinum* or *Gloeophyllum adoratum* or *Gl. protactum* or *Gloeophyllum sepiarium* or *Gl. Trabeum*; *Lentinus* such as *Lentinus cyathiformes* or *Lentinus edodes* or *Lentinus lepideus* or *Lentinus grinus* or *L. squarrolosus*; *Paxillus* such as *Paxillus panuoides*; *Pleurotus* such as *Pleurotis ostreatus*; *Poria* such as *Poria monticola* or *Poria placenta* or *Poria vaillantii* or *Poria vaporaria*; *Serpula* such as *Serpula himantoides* or *Serpula lacrymans*; *Stereum* such as *Stereum hirsutum*; *Tyromyces* such as *Tyromyces palustris*; *Deuteromycetes*; *Alternaria* such as *Alternaria tenius*; *Cladosporium* such as *Cladosporium herbarum*.

In addition to the aforementioned active compounds A) and B), the compositions according to the present invention optionally may further contain other active compounds C), e.g. other microbiocides, in particular fungicides, and also insecticides. The following active compounds C) are mentioned as optional insecticides:

Phosphoric esters such as azinphos-ethyl, azinphos-methyl, 1-(4-chlorophenyl)-4-(O-ethyl,S-propyl)phosphoryloxypyrazole, chloropyrifos, coumaphos, demeton, demeton-S-methyl, diazinon, dichlorvos, dimethoate, ethoprophos, etrimfos, fenitrothion, fenthion, heptenophos, parathion, parathion-methyl, phosalone, phoxim, pirimiphos-ethyl, pirimiphos-methyl, profenofos, prothiofos, sulfprofos, triazophos and trichlorophon;

Carbamates such as aldicarb, bendiocarb, 2-(1-methylpropyl)-phenyl methylcarbamate, butocarboxim, butoxycarboxim, carbaryl, carbofuran, carbosulfan, cloethocarb, isoprocarb, methomyl, oxamyl, pirimicarb, promecarb, propoxur and thiodicarb;

Organosilicon compounds, preferably dimethyl(phenyl)silylmethyl 3-phenoybenzyl ethers, such as dimethyl-(4-ethoxyhpenyl)silylmethyl 3-phenoxybenzyl ether or (dimethylphenyl)-silyl-methyl 2-phenoxy-6-pyridylmethyl ethers such as, for example, dimethyl(9-ethoxy-phenyl)silylmethyl 2-phenoxy-6-pyridylmethyl ether or [(phenyl)-3-(3-phenoxyphenyl)-propyl](dimethyl)-silanes, such as, for example, (4-ethoxyphenyl)-[3-(4-fluoro-3-phenoxy-phenyl-propyl]dimethyl silane.

Pyrethroids, such as allethrin, alphamethrin, bioresmethrin, byfenthrin, cycloprothrin,

cyfluthrin, decamethrin, cyhalothrin, cypermethrin, deltamethrin, alpha-cyano-3-phenyl-2-methylbenzyl 2,2-dimethyl-3-(2-chloro-2-trifluoro-methylvinyl)cyclopropanecarboxylate, fenpropathrin, fenfluthrin, fenvalerate, flucythrinate, flumethrin, fluvalinate, lambda cyhalothrin, gamma cyhalothrin, permethrin, resmethrin and tralomethrin;

Arylpyrazoles such as fipronil.

Nitroimines and nitromethylenes, such as imidacloprid, thiamethoxam, thiacloprid, acetamiprid and clothianidin.

The total amount of active substance A), or mixture of substances A), B) and optionally C) employed depends on the species and the occurance of the microorganisms, the microbial count and the medium. The optimum dosage rate for use can be determined in each case by test series. In general, however, it suffices to employ 0.001 to 20% by weight, preferably 0.05 to 10% by weight, of the active compounds based on the material to be protected.

In one embodiment, synergistic mixtures of the active compounds A) and B) are employed in the compositions and methods according to the present invention such that a synergistic antimicrobial effect is obtained upon application. In particular, it is contemplated that in the compositions to be used directly, the concentration of fludioxonil (A) taken as base equivalent, may range from 10 to 15000 ppm, in particular from 50 to 12000 ppm or from 50 to 6000 ppm, more in particular from 100 to 3000 ppm; and the concentration of compound (B) taken as base equivalent is contemplated to range from 10 to 15000 ppm, in particular from 50 to 10000 ppm or from 100 to 8000 ppm, more in particular from 200 to 6000 ppm. In many instances said compositions to be used directly can be obtained from concentrates upon dilution with aqueous or organic media, such concentrates also being intended to be covered by the term composition as used in the definitions of the present invention. The content of the active compounds in the above-indicated compositions is from 0.01 to 95%, preferably from 0.1 to 50% more preferably from 0.1 to 20% and in particular from 0.2 to 15% by weight. The compositions according to the invention are preferably used in the form of solutions, suspensions or microemulsions.

The ratio between the active compounds A) and B) in said synergistic compositions may vary within relatively broad ranges and will be dependent on the application

aimed at. However, for practical reasons, a quantitative ratio such that a synergistic antimicrobial effect is obtained can be selected. Particularly, it is contemplated that the weight ratio between the active compounds A) and B) may be situated between 50:1 and 1:50, more particularly between 20:1 and 1:20. Preferably said ratio is between 10:1 and 1:10, more preferably between 5:1 and 1:5.

These ratios are not intended to limit the nature of the invention and may provide a suitable means for tailoring the efficiency of broad classes of antimicrobial compositions which may require a combination of these active compounds A) and B).

The active compound A), or mixtures thereof with at least one of the active compounds B), and optionally with at least one compound C), can be in the form of water-dilutable concentrations which are then applied in a customary manner in the form of a dilution with water, or in the form of so-called tank mixes which are prepared by concomitant dilution of the separately formulated components with water immediately prior to application. They can also be applied in the form of aqueous ready-for-use solutions or are used in unmodified form or together with adjuvants conventionally employed in the art of formulation. The formulations, i.e. the compositions, preparations or mixtures containing the active compounds and, where appropriate, a solid or liquid adjuvant, are prepared following art-known procedures, e.g. by homogeneously mixing and/or grinding the active compounds with extenders, e.g. solvents, solid carriers and, where appropriate, surface-active compounds (surfactants), to emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations in e.g. polymer substances. As with the nature of the compositions, the methods of application, such as spraying, atomizing, dusting, scattering or pouring, brushing, dipping, soaking or impregnating, are chosen in accordance with the intended objectives and the prevailing circumstances.

For example, in order to protect a locus such as wood from decay it can treated with the active compound A), or mixtures thereof with at least one of the active compounds B) in synergistic compositions according to the present invention. Such treatment is applied by several different procedures such as, for example, by treating the wood in closed pressure- or vacuum systems, in thermal- or dip systems and the like, or by a wide variety of surface treatments, e.g. by brushing, dipping, spraying or soaking the wood with a formulation containing the wood-preserving agents A) and B).

Those skilled in the art will recognize that mixtures or combinations of the active compound A) with at least one of the active compounds B) of the present invention may be added to a locus sequentially, simultaneously, or may be combined before being added to the locus. Sequential applications include so-called split applications where the active compounds are applied up to a few days one after the other.

The abovementioned formulations and compositions can be prepared in a manner known per se, for example by mixing the active compound(s) with a suitable carrier such as at least one solvent or diluent, emulsifier, dispersant and/or binder or fixative, water repellant, optionally siccatives, antifreeze agents, antifoams and UV stabilisers, and optionally colourants and pigments as well as other processing auxiliaries.

Suitable solvents or diluents are organochemical solvents or solvent mixtures and/or a polar organic solvent or solvent mixture and/or an oily or oil-type organochemical solvent or solvent mixture and/or water, if appropriate together with an emulsifier and/or wetting composition. Customary water-insoluble oily or oil-type solvents of low volatility which are preferably used are the vegetable oils, methylated vegetable oils, particular mineral oils/mineral-oil-containing solvent mixtures or their aromatic fractions. White spirit, petroleum or alkylbenzenes, and additionally spindle oil and monochloronaphthalene may be mentioned as being preferred. The boiling ranges of these solvent (mixtures) of low volatility cover a range of approximately 170° C. to not more than 350° C.

The above-described oily or oil-type solvents of low volatility can be replaced partially by more volatile organochemical solvents.

To prepare a wood preservative, some of the above described solvent or solvent mixture is preferably replaced by a polar organochemical solvent or solvent mixture. Solvents which are preferably used are those containing hydroxyl groups, ester groups, ether groups or mixtures of this functionality. Examples which may be mentioned are esters or glycol ethers. Binders are to be understood according to the invention as being synthetic resins, binding drying oils, for example based on acrylic resins, vinyl resins, polyester resins, polyurethane resins, alkyd resins, phenol resins, hydrocarbon resins or silicone resins which can be diluted with water or are soluble, dispersible or emulsifiable in organochemical solvents. The binder used can be employed as a solution, emulsion or dispersion. Mixtures of alkyd resins and drying

vegetable oil are preferably used. Alkyd resins with an oil content of between 45 and 70% are particularly preferred.

All or some of the abovementioned binder can be replaced by a fixative (mixture) or a plasticiser (mixture). These additives are intended to prevent volatilization of the active compound as well as crystallisation or precipitation. They preferably replace 0.01 to 30% of the binder (based on 100% of the binder used).

The plasticisers are from the chemical classes of the phthalic esters such as dibutyl, dioctyl or benzyl butyl phthalate, phosphoric esters such as tributyl phosphate, adipic esters such as di-(2-ethylhexyl) adipate, stearates such as butyl stearate and amyl stearate, oleates such as butyl oleate, gylcerol ethers or higher-molecular-weight glycol ethers, glycerol esters as well as p-toluenesulphonic esters.

Fixatives are based, from the chemical point of view, on polyvinyl alkyl ethers such as, for example, polyvinyl methyl ether, or ketones such as benzophenone or ethylenebenzophenone.

The preferred solvent or diluent is water, if appropriate in a mixture with one or more of the abovementioned solvents or diluents, emulsifiers and dispersants.

FORMULATION EXAMPLES

In the examples which follow (% = per cent by weight). The examples are intended to illustrate and not limit the invention, "active compound(s)" being understood as meaning fludioxonil or a mixture of fludioxonil with the at least one of active compounds (B) in a mixing ratio of from 5:1 to 1:5.

Example F1: Emulsifiable concentrates	a)	b)	c)
Active Compound(s)	25%	40%	50%
calcium dodecylbenzenesulfonate	5%	8%	6%
castor oil polyethylene glycol ether	5%	-	-
tributylphenol polyethylene glycol ether	-	12%	4%
Cyclohexanone	-	15%	20%
xylene mixture	65%	25%	20%

Emulsions of any desired concentration can be prepared from this concentrate by dilution with water, and can be employed in materials protection applications.

Example F2: Dusts	a)	b)
Active Compound(s)	5%	8%
Talc	95%	-
Kaolin	-	92%

Ready-to-use dusts are obtained by mixing the active ingredients with the carrier and grinding the mixture in a suitable mill.

Example F3: Wettable powders	a)	b)	c)
Active Compound(s)	25%	50%	75%
sodium lignosulfonate	5%	5%	-
sodium laurylsulfate	3%	-	5%
sodium diisobutylnaphthalenesulfonate	-	6%	10%
octylphenol polyethylene glycol ether	-	2%	-
highly dispersed silicic acid	5%	10%	10%
Kaolin	62%	27%	-

The active ingredient is mixed thoroughly with the additives and the mixture is ground thoroughly in a suitable mill affording wettable powders which can be diluted with water to give suspensions of any desired concentration.

Example F4: Suspoemulsions	a)
Active Compound(s)	22.5%
sulfated nonylphenol (polyoxyethylene condensate)	0.1%
phosphated tristyrylphenol (polyoxyethylene condensate)	4%
sodium lignosulfonate (polyoxyethylene condensate)	2%
NaOH (50%)	0.1%
silicone defoaming agent	0.1%
Glycerin	20%

xanthan gum	0.2%
Water	51%

This formulation is suitable for mixtures of solid and liquid active ingredients. The solid active ingredient(s) are mixed thoroughly with a portion of the emulsifiers and water and the mixture is ground thoroughly in a suitable mill. Another portion of the emulsifiers and water are mixed with the liquid active ingredient(s). The two mixtures are combined along with any other inert ingredients (such as thickeners, etc.) that are to be used in the formulation.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined by the appended claims.

We claim:

1. A method of controlling harmful microbial growth on or in engineering materials, which comprises applying an antimicrobially effective amount of an antimicrobial composition that comprises A) fludioxonil to the engineering material to be treated.

2. The method according to claim 1, wherein the antimicrobial composition further comprises B) at least one compound selected from azaconazole, bitertanol, bromuconazole, cyproconazole, diclobutrazol, difenoconazole, diniconazole, diniconazole-m, epoxiconazole, etaconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, furconazole, furconazole-cis, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole fumarate, paclobutrazol, pefurazoate, penconazole, propiconazole, prothioconazole, quinconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, and uniconazole-p.

3. The method according to claim 1, wherein the active compounds A) and B) are employed in a ratio by weight of from 5:1 to 1:5.

4. The method according to claim 1, wherein the antimicrobial composition further comprises C) an insecticide selected from imidacloprid, thiamethoxam and fipronil.

5. An antimicrobial composition which comprises A) fludioxonil in combination with B1) at least one compound selected from azaconazole, bitertanol, bromuconazole, diclobutrazol, diniconazole, diniconazole-m, epoxiconazole, etaconazole, fenbuconazole, flusilazole, flutriafol, furconazole, furconazole-cis, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole fumarate, paclobutrazol, pefurazoate, penconazole, propiconazole, prothioconazole, quinconazole, simeconazole, tetraconazole, triadimefon, triadimenol, uniconazole, and uniconazole-p.

6. The antimicrobial composition as claimed in claim 5, which comprises the active compounds A) and B1) in a ratio by weight of from 5:1 to 1:5.

7. The antimicrobial composition as claimed in claim 5, wherein B1) is propiconazole.

8. The antimicrobial composition as claimed in claim 5, which further comprises C) an insecticide selected from imidacloprid, thiamethoxam and fipronil.

9. A method of controlling harmful microbial growth on or in industrial materials, which comprises applying an antimicrobially effective amount of the antimicrobial composition according to claim 5 to the industrial material to be treated.

10. The method according to claim 9, wherein the industrial material is selected from leather, leather products, wood and wood products.

11. The method according to claim 9, wherein the industrial material is an engineering material.

12. A method of controlling harmful microbial growth on or in industrial materials, which comprises applying an effective antimicrobial amount of the antimicrobial composition according to claim 1 to the industrial material to be treated.

13. A method of preserving wood or wood products which comprises treating the wood or wood products with an antimicrobially effective amount of an antimicrobial composition consisting essentially of fludioxonil and a carrier.

14. A method of controlling harmful microbial growth on or in engineering materials, which comprises treating the engineering materials with an antimicrobially effective amount of an antimicrobial composition comprising fludioxonil, tebuconazole and a carrier.

15. A method of controlling harmful microbial growth on or in industrial materials, which comprises treating the industrial materials with an antimicrobially effective amount of an antimicrobial composition comprising fludioxonil in combination with B2) at least one compound selected from cyproconazole, propiconazole, triticonazole and fluquinconazole.

16. The method according to claim 15, wherein the active compounds A) and B2) are employed in a ratio by weight of from 5:1 to 1:5.

17. The method according to claim 15, wherein the antimicrobial composition further comprises C) an insecticide selected from imidacloprid, thiamethoxam and fipronil.

18. The method according to claim 15, wherein the industrial material is selected from leather, leather products, wood and wood products.

19. The method according to claim 15, wherein the industrial material is an engineering material.

20. The method according to claim 15, wherein wherein B2) is selected from propiconazole and cyproconazole.

ABSTRACT

The present invention relates to the use of (A) the compound 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile (fludioxonil) as a microbicide for the protection of industrial materials, to synergistic mixtures containing such compound, and to the use of such mixtures for the protection of industrial materials.